

π Electronic Distribution, Charge Transfer and Intensities of Infrared Absorption Bands in Borazine

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The π charge distribution of borazine is obtained by an LCAO calculation, modifying slightly an approximation already applied to pyridine. A simple method is proposed for the comparison of the relation between the charge transfer as calculated in the NH and BH bonds with the experimental relation between the intensities of the corresponding absorption bands in the infrared spectrum. The influence of the π distribution over the σ skeleton must be considered in order to obtain a better agreement with experimental data.

On obtient la distribution de charge π de la borazine par moyen d'un calcul LCAO, en modifiant légèrement une approximation appliquée auparavant à la pyridine. On propose une méthode simple pour comparer la relation entre la transférence de charge calculée dans les liaisons NH et BH avec la relation expérimentale entre les intensités des bandes d'absorption correspondantes du spectre infrarouge. On doit considérer l'influence de la distribution π sur le squelette σ pour améliorer l'accord avec les données expérimentales.

Die π -Elektronendichte in Borazol wird mit einem LCAO-Verfahren berechnet, das mit Ausnahme einer geringfügigen Modifikation schon auf Pyridin angewandt worden ist. Mit Hilfe einer einfachen Methode werden die berechneten Ladungsübergänge in der NH und BH Bindung mit den entsprechenden Absorptionsschwingungsbanden verglichen. Der Einfluß der π -Elektronenverteilung auf das σ -Gerüst wird berücksichtigt.

Introduction

In this paper, an approximation for semiempirical parameters in LCAO calculation, modifying slightly the one already used for pyridine [14], is applied to borazine. We are interested in testing this approximation for borazine, wherein the difficulty in the selection of the parameters is well known.

By using the principle of electronegativity equalization, we have calculated the charge transferred in the BH and NH bonds of borazine, by means of FERREIRA's formulae [5].

The results coming out from this calculation may be compared with experimental data for relative intensities of infrared bands. A simple method is provided for this. In fact, the integrated intensity of the infrared absorption band of a diatomic molecule is proportional to $(\delta\mu/\delta r)^2$, where μ is the dipole moment and r the interatomic distance. Assuming that for small displacements the transferred charges q remains constant [5], we can write $\delta\mu/\delta r = q$; the intensity will be, therefore, a measure of the charge transferred. The frequently used approximation

of bond moments additivity allows to apply the statement to polyatomic molecules, specially to vibrations which involve deformations of only one kind of bonds.

We shall consider the influence of the π distribution over the σ skeleton in a way very simple, although sufficient to obtain a fair agreement with experimental data.

Parameters and LCAO Calculation

It is usually accepted that, in a molecule such as borazine, the nitrogen delivers negative charge to boron [3]. We shall then suppose, as a mere calculation hypothesis, that we are dealing with N^+ and B^- and not with neutral atoms.

We shall take for the coulomb (α) integrals that appear in the simple LCAO method [14]:

$$\alpha_{N^+} = - (I_{N^+} + E_{B^-}) = - 28.95 \text{ eV}$$

$$\alpha_{B^-} = - (I_{B^-} + E_{N^+}) = - 14.51 \text{ eV}$$

where I and E are ionization energies and electron affinities of B^- and N^+ , after the data reported by DAVIES [3]. As expected, α_{N^+} is much lower than α_{B^-} .

For the resonance integrals (β) we shall use the expression

$$\beta_{ab} = - S_{ab}(E_a + E_b)$$

S_{ab} being the overlap integral of the π orbitals centered in atoms a and b . This expression differs from that previously used [14] in the factor S_{ab} . It gives here direct account of the fact that β must depend on the interatomic distance.

In the calculation of S_{ab} we use, as before, KOHLRAUSCH's nuclear effective charges [8]. With these nuclear charges, and considering the screening constant of the respective differentiating electron [5], we obtain for B^- and N^+ :

$$Z_{B^-}^* = 1.1; \quad Z_{N^+}^* = 3.03 .$$

We are taking into account all the resonance integrals and all the overlap integrals, including those between non-neighboring atoms (see Tab. 1).

The following energy levels are obtained:

$$\varepsilon_1 = - 1.3742 \text{ a.u.}; \quad \varepsilon_2 = - 1.0866 \text{ a.u.}$$

$$\varepsilon_3 = - 0.6682 \text{ a.u.}; \quad \varepsilon_4 = 0.2592 \text{ a.u.}$$

of which ε_1 and ε_3 are doubly degenerate.

Table 1. *Overlap Integrals (S_{ab}) in borazine, with Kohlrusch's nuclear effective charges and Resonance Integrals (β_{ab})*

a, b	S_{ab} (a.u.)	β_{ab} (eV)
1,2	0.3216	-4.32
1,3	0.0418	-1.12
1,4	0.1068	-1.39
2,4	0.5570	-0.11

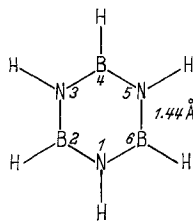


Fig. 1: Labelling of atoms in borazine

Borazine belongs to the symmetry group D_{3h} ; the corresponding molecular orbitals ψ are, for the fundamental state:

$$\psi_1 = 0.428 (2\varphi_2 - \varphi_4 - \varphi_6) - 0.217 (2\varphi_5 - \varphi_1 - \varphi_3)$$

$$\psi'_1 = -0.377 (\varphi_1 - \varphi_3) + 0.742 (\varphi_4 - \varphi_6)$$

$$\psi_2 = 0.503 (\varphi_1 + \varphi_3 + \varphi_5) + 0.066 (\varphi_2 + \varphi_4 + \varphi_6) .$$

φ being the atomic orbitals centered according to the labelling in Fig. 1. We see that the orbitals belonging to the lowest energy level have nodes. This does not happen in the Hückel approximation. But there is no reason to believe that the same behaviour should occur applying another approximation. It is known [2] that, if the commutator $[H, S]$ (H , hamiltonian operator) is zero, the treatment considering overlap should give the same results as the Hückel approximation. But we have already shown that the use of Kohlrausch's charges (due to the fact that their overlap values are larger than Slater's overlaps) together with our approximation [14], leads to commutator eigenvalues which cannot be neglected. The results with and without overlap are in this case quite different. The commutator $[H, S]$ must therefore rule the behaviour of each approximation. We have partially analyzed this question elsewhere [9].

With these orbitals, we calculated the charges q (Tab. 2) and bond orders p by using CHIRGWIN and COULSON's formulae [2].

Literature on the borazine molecule reports for q_B widely spread data ranging from 0.24 [17] up to 0.893 [3] (Tab. 2). Our q_B value is of the expected order,

Table 2
Charge distribution in borazine obtained by different authors

	q_1	q_2
WATANABE et al. [17]	1.76	0.24
CHALVET et al. [1]	1.522	0.478
KOBAYASHI*	1.48	0.52
DAVIES [3]	1.107	0.893
This work	1.121	0.879

(WATANABE et al. use LCAO, trying different values for the parameter $d = (\alpha_N - \alpha_B)/2\beta$. The other authors apply different self-consistent methods).

* As reported by WATANABE [17].

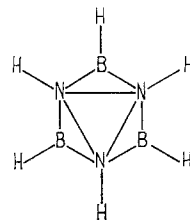


Fig. 2: A possible structure for borazine

considering the similarity between the benzene and borazine spectra [11]. In order to obtain equivalent results using Pople's self-consistent method, DAVIES [3] has been forced to abandon the physical meaning of the coulomb parameter. In azines, this parameter has been successfully identified with the valence state ionization potentials of free atoms [4].

Our p values are:

$$p_{12} = 0.6600; \quad p_{13} = 0.3363; \quad p_{14} = -0.4208; \quad p_{24} = -0.3363.$$

Other values found in the literature for p_{12} are, for example, RĚCTOR et al. 0.15 [13]; WATANABE's 0.45 [17]; DAVIES' 0.66 [3]. With the last one, equal to ours, DAVIES obtains a bond length of 1.42 Å, within the experimental value 1.44 ± 0.02 Å. The relative values of p_{13} and p_{12} (even if this comparison is not at all direct, for p_{12} is p_{B-N^+} , and p_{13} is $p_{N^+N^+}$) suggest that, besides the Kekulé structures, there may exist a structure of the type shown in Fig. 2. This structure is consistent with the one which has a lone pair in each nitrogen atom, which makes an important contribution to the normal state [10]. Compounds possessing this triborine-triamine structure, must react with HCl [13]. It is well known that this

reaction actually takes place in borazine; it is even used for its quantitative determination [16].

Charge Transfer and Infrared Spectrum Bands

In order to compare the charge transferences and the intensity of the bands, it is convenient to make the following considerations. The 3483 cm^{-1} absorption band of borazine corresponds to a normal mode which involves only stretchings of the NH bonds. The 2527 cm^{-1} band is geometrically similar to the former and involves only stretching of the BH bonds (Fig. 3). It is reasonable to assume, therefore, that the ratio of the total dipole moment changes in both vibrations is the same as the ratio of the respective bond dipole moment changes.

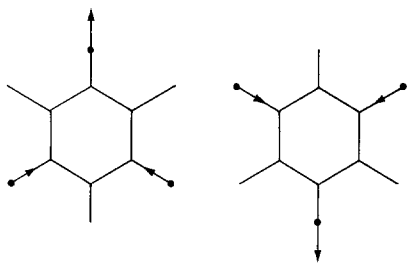


Fig. 3. The two similar normal vibration modes of NH and BH bonds

The charge transference in a given bond ab is calculated by the formula [5]:

$$q_{ab} = \frac{X_b - X_a}{\sum \Delta X^- + \sum \Delta X^+}$$

X_a , X_b being the electronegativities of atoms a and b ; ΔX^- , ΔX^+ the change which would be produced in electronegativity by the transference of a whole electronic charge.

For the calculation of the ΔX , we require the knowledge of the electronegativity of C^+ and C^- [5], which we obtain in the following way. PRITCHARD and SUMMER [12] assert that the energies of an element in its different ionization states may be approximated by a parabola. HINZE and JAFFÉ [6] have also mentioned this way of calculating X for ions. Using the parabolic relation through the points corresponding to C^{2+} and C^{2-} we obtain:

$$X_{N^+} = 6.71; \quad X_{B^-} = 0.17; \quad \Delta X_{N^+}^- = 5.94; \quad \Delta X_{B^-}^+ = -0.326.$$

Therefore the charge transference we are looking for would be:

$$q_{N^+H} = 0.52; \quad q_{B^-H} = 0.52.$$

It would then result, in this approximation, that the NH and BH bands have the same intensity. However we have until now neglected the influence of the π distribution over the σ skeleton [14]. The electron π charge distribution changes the electronegativities of B^- and N^+ to:

$$X_{N^+} = 5.99; \quad X_{B^-} = 0.13.$$

Therefore the charge transfer becomes:

$$q_{N^+H} = 0.436; \quad q_{B^-H} = 0.619.$$

Those charges throw an intensity relation BH band/NH band of 2.0. The experimental value is 3.5 [15]. As in a preliminar calculation assigning bands only the order of magnitude matters, the agreement is satisfactory.

The apparent integrated absorption intensity of the 3483 and 2523 cm^{-1} bands of borazine were measured with a Beckmann IR9 spectrophotometer, using a spectral slit width of 0.5 cm^{-1} . The areas under the curve in the linear absorbance-linear wave number spectra were determined for carefully purified samples contained in a 10 cm gas cell at pressures which were made to vary from 1 to 100 mm of Hg.

In short

These results, in fair agreement with experiment, indirectly confirm the supposition of the polarity B-N⁺ in the bond, according to ordinary valence theory, and in opposition to the distribution suggested by HOFFMANN [7]. They indicate too that the approximation applied to the LCAO parameters, and KOHLRAUSCH's nuclear effective charges, may be also used with some confidence in inorganic systems.

Finally it may be remarked that a simple way of comparing relations between charge transferences and relative intensities of infrared bands is provided, under conditions similar to those mentioned above.

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